GLASS TRANSITION TEMPERATURES OF POLY(METHYL METHACRYLATE) PLASTICIZED WITH LOW CONCENTRATIONS OF MONOMER AND DIETHYL PHTHALATE

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SYNOPSIS

The effect of low plasticizer concentrations on the glass transition temperature of poly(methyl methacrylate) (PMMA) has been studied experimentally for diethyl phthalate (DEP) and methyl methacrylate (MMA) as plasticizers. Volume dilatometry, differential thermal analysis, and a torsional pendulum were used to determine glass transition temperatures. The monomer plasticized PMMA samples were prepared by polymerizing MMA to a limiting conversion which was found to depend primarily on temperature. At temperatures slightly above the glass transition temperature of a MMA-PMMA system, a polymerization reaction occurred at a rate rapid enough to complicate the interpretation of the dilatometric and differential thermal analysis methods for determining the glass transition temperature. However, the torsional pendulum method could be used since it did not require measurements to be made at temperatures where polymerization could occur. The differential thermal analysis results showed that the temperature at which the polymerization reaction was first detectable was related to the glass transition temperature of the MMA-PMMA solution. The measured glass transition temperatures were compared with the predictions of the theories of Fox, Kelley, and Bueche and Dimarzio and Gibbs on the effect of plasticizer concentration on the depression of the glass transition temperature.

INTRODUCTION

The exposure of polymers to ultraviolet and other higher energy radiation fields may initiate decomposition reactions that lead to the formation of low molecular weight products. These products of decomposition, if they remain in the bulk material, can modify the mechanical properties of polymers by acting as plasticizers. In an earlier study[1] an analytical expression was developed which related the yield stress of poly(methyl methacrylate) (PMMA) at temperatures below the glass transition temperature (T_g) to strain rate, test temperature, and plasticizer content. In the present study, methods of measuring or calculating the glass transition temperatures of plasticized PMMA systems were investigated as part of a continuing program to relate the mechanical behavior of various polymeric materials to their glass transition temperatures. During this study, attempts to measure T_g for the PMMA-MMA system by the accepted dilatometric method were complicated by polymerization in the region of the glass transition temperature. This made the determination of T_g from the dilatometric data potentially unreliable. For this reason, differential thermal analysis (hereafter referred to as DTA) and torsional pendulum methods of measuring glass transition temperatures were also evaluated. Glass transition temperatures measured by these two methods were related to the dilatometrically determined T_g for a PMMA-DEP system which is free of the complications of polymerization. This relation is then used to determine the "true" dilatometric T_g of the PMMA-MMA system from the glass transition temperatures measured by the torsional pendulum method and by DTA. Finally, the Fox,[2,3] Kelley-Bueche,[4]

and Dimarzio-Gibbs[5] relations of glass transition temperature depression due to plasticizer content are compared with the measured T_g.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) obtained from the Rohm and Haas Company was washed with 5% NaOH and with water to remove the inhibitor, and was then dried and distilled. A middle fraction was collected for use in the preparation of polymer samples. Gas chromatography showed that the distilled monomer was free of impurities.

Diethyl phthalate (DEP) (Eastman, White Label) was used as received, as was α, α', azobisisobutyronitrile (AIBN) (DuPont's Vazo).

Preparation of Diethyl-Phthalate- and Monomer-Plasticized Poly(Methyl Methacrylate)

Diethyl Phthalate. PMMA samples containing 3.0%, 3.6%, 8.0%, and 16.0% by weight of DEP were prepared by solution polymerization as follows: Methyl methacrylate containing 0.5 part per hundred of AIBN was mixed with the desired weights of DEP and the mixture placed in 15-mm glass-tube ampoules. containing a constriction. The mixtures were carefully degassed on a high vacuum rack as described by Morton[6] and sealed off under a pressure of 10^{-5} torr. The polymerization ampoules were placed in a thermostat at 40° C for 24 hrs. and the temperature then was raised in 15° C increments each day until it reached 130° C. Unusable samples containing bubbles were produced if polymerization was attempted at a

higher initial temperature or if the polymerization temperature was raised more rapidly. This might be explained by the Trommsdorff effect.[5] Samples prepared in this way showed no evidence of unpolymerized monomer when examined by I. R. analysis. Each cylindrical sample was machined to give specimens for the three methods of measuring glass transition temperatures.

Monomer. Monomer plasticized samples were obtained by the bulk polymerization of MMA conducted at temperatures between 30° and 100° C. Monomer containing 0.5% of AIBN was degassed on a high vacuum rack and sealed in a 500-ml flask containing a "break seal" outlet tube. The monomer-initiator solution was distributed and sealed into eight 15-mm tubes by a high vacuum technique described by Morton, et al.[6] This was done to insure that all of the polymerized samples would have the same concentration of AIBN. All tubes were allowed to polymerize for 24 hrs. at 40° C. Each tube was then thermostated for 4 to 7 days at temperatures between 30° and 120° C. It was found that with this technique there was a limit for conversion of monomer to polymer which depended on the final temperature of polymerization. The cylindrical samples obtained were machined to give specimens for each of the three methods of measuring glass transition temperatures.

Characterization of DEP-PMMA and MMA-PMMA Systems

I. R. Analysis Methods. An infrared method of analysis was used for determining the amount of monomer in the PMMA systems. The infrared spectra of solutions of PMMA and MMA in chloroform were obtained with a Beckman I. R. 8 in the region of 6.1 microns where the monomer has an

absorption band (carbon-carbon double bond) which is not observed in the polymer. Chloroform is used since it is essentially transparent at 6.1μ. The solutions were run in cells of 1-mm path length with a matched cell containing chloroform in the reference beam of the instrument. A calibration curve relating solution optical density at 6.1μ to concentration of monomer was obtained from the spectra of eleven synthetic mixtures prepared by weighing and mixing pure MMA and PMMA to simulate samples containing from 1% to 12% MMA. The solute volume was taken into account to determine the concentration of the solution. Total sample concentrations were chosen to give I_o/I values in the range 1.3 to 3.0. The use of high sample concentrations (chloroform solution concentrations of up to 0.08 g/ml could be used) and long cell path lengths made this method quite accurate for determining the monomer. Results were reproducible to ±5% of the monomer content. Quantitative results on samples containing less than 0.5% monomer could not be obtained because solutions of the required high sample concentration were too viscous to be transferred to the absorption cell.

The Dependence of Polymerization Rate on Temperature at High Conversion. To demonstrate that the concentration of monomer would remain constant during the measurement of the glass transition temperature, the rate of bulk polymerization of MMA at high conversions was briefly investigated. The results for a polymerization conducted at 55° C are shown in Figure 1 where percent unpolymerized MMA is plotted against the elapsed time. The experiment was conducted with nine ampoules (10 mm dia.) prepared from the same solution of 0.5% AIBN. The ampoules were treated as described for the preparation of monomer

plasticized PMMA; that is, they were placed in a 40° C bath for [illegible] and then thermostated at 55° C. Ampoules were opened periodically and analyzed for MMA by the previously described I. R. method. Figure 1 shows that after 96 hrs. at 55° C, the rate of polymerization has decreased to about 0.01% per hr. Two of the samples carried through the rate experiment at 55° C were allowed to continue polymerizing at 80° C and the polymerization rate increased by a factor of about 10. The rate of polymerization of samples polymerized at the other temperatures also decreased to a low value after 4 days. The limiting conversion at which this low value was attained was found to depend on the polymerization temperature and on the amount and type of initiator employed for the polymerization. The polymerization temperatures, together with limiting conversions obtained using monomer containing 0.5% AIBN, are given in columns 2 and 3 of Table I.

Molecular Weight Determinations. The viscosity average, $\bar{M}_v$, and the number average, $\bar{M}_n$, molecular weights of three polymers prepared by the methods described, were determined and the results are summarized in Table II. A Cannon-Ubbelohde dilution viscometer, having a flow time for benzene of 190 sec., was used to obtain the viscosity data. The viscosity average molecular weights were obtained by use of the equation relating intrinsic viscosity (η) of PMMA solutions in benzene at 30° C to $\bar{M}_v$ reported by Hwa.[8] This equation is

$$(\eta) = 5.3\times10^{-5}\ \bar{M}_v^{0.78}$$

Number average molecular weights were obtained with a Mechrolab Model 501, high-speed membrane osmometer at 37° C. Toluene was used as the solvent.

Stereoisomeric Structure - N.M.R. Spectra. The N.M.R. spectra of three of the PMMA samples prepared by polymerization at different temperatures were obtained with a Varian A-60 N.M.R. spectrometer. The interpretation of the N.M.R. spectrum of PMMA has been worked out by Bovey and Tiers.[9] Spectra were obtained at 90° C with solutions of PMMA in deutero-chloroform (conc. about 3 g/100 ml). The results are reported in Table II as the ratio of the area, P_h, of the heterotactic peak (9.0τ) to the area, P_s, of the syndiotactic peak (9.14τ) to facilitate comparison with the results of Fox and Schnecko.[10] The definition of τ is given in most N.M.R. texts.[11]

Methods For Determining Glass Transition Temperature

Dilatometric Method. The method described by Bekkedahl[12] for measurement of dilatometric glass transition temperature was used. Both mercury and silicone oil were used as confining liquids. The dilatometers were constructed from 2-mm true-bore capillary tubes sealed to 15-mm tubing. Cylindrical test specimens weighing from 8 to 15 g were employed. The oil bath thermostat was controlled to ±0.1° C. Temperature was raised or lowered in intervals of about 5° to 10° C. Equilibration times of 30 min. were allowed after every temperature change.

Differential Thermal Analysis Method. A schematic diagram of the DTA heating block used in this study is shown in Figure 2. The overall design of the DTA system was similar to the one described by Strella.[13] The aluminum heating block was lowered into the center of a standard Marshall furnace. The furnace heating rate was controlled by

a motor-driven variac which produced a $5 \pm 0.5^{\circ}$ C/min. temperature increase in the heating block. The specimens were machined into 0.[illegible] ± 0.010 in. diameter and 0.135 ± 0.010 in. thick disks. One disk was placed in the specimen cavity and the specimen temperature and differential temperature thermocouples were positioned on the disk as shown in Figure 2. Then a second disk was placed over the first and the upper part of the heating block was lowered and clamped with a force sufficient to insure good contact between the flat sides of the disk and the heating block and also between the thermocouples and the disks. MgO powder, which was used as a reference material, was tamped around the thermocouples on the reference side. The specimen-temperature thermocouple was connected to the X axis of an X-Y recorder (Moseley 5-S). The differential-temperature thermocouple was connected to an indicating millivolt potentiometer which is essentially a high gain, stable amplifier. The amplified differential-temperature signal was then sent to the Y axis of the recorder.

Dynamic Mechanical Method (Torsional Pendulum). A schematic diagram of the torsional pendulum used in this study is shown in Figure 3. The assembly was mounted on the top panel of an air bath temperature control chamber (Statham SD-8). The rotary variable differential transformer (RVDT) and the inertial disk were mounted exterior to the chamber. The RVDT was mounted on a teflon diaphragm which restrained it from rotating but allowed a small amount of tilting. The hinged lower support arm assured that the axial tension in the specimen was negligible. Specimens were approximately 1/32 in. thick, 1/4 in. wide, and 2 in. long between the grip faces. The inertia disk used was aluminum 5.81 in. in diameter

and 0.0650 in. thick. The over-all oscillator system inertia was 2097 gr cm^2. The RVDT (Schaevitz type R4BSS) was used with a demodulator (Schaevitz DMPS-3). The damped response curve was recorded on an oscillograph (C.E.C. Type S-119). The oscillation frequency for this combination of specimen size and inertial disk was approximately 2 cycles per second at temperatures below the glass transition region and decreased to 1/2 cycle per second in the glass transition region. As will be discussed, the glass transition temperature was defined as the temperature at which the damping reaches a specified level. Individual data points for a given damping spectrum were collected at 10-min. intervals. The temperature was raised 10° F after each run. The furnace temperature rose in approximately 1 min. to the set temperature, thus allowing 9 min. for the temperature to equilibrate in the specimen.

RESULTS

Glass Transition Temperature Measurements on DEP Plasticized PMMA

Typical dilatometer curves for DEP plasticized PMMA are shown in Figure 4. The ordinate is the height of the mercury in the capillary tube and the abscissa is the bath temperature. The standard procedure[12] was used for determining the glass transition temperature. The procedure consists of approximating the curves above and below the glass transition region by straight lines. The glass transition temperature defined by the intersection of these two lines was found to be reproducible within ±2° C.

Typical differential thermal analysis curves for PMMA-DEP are shown in Figure 5. The ordinate is the temperature difference between the specimen and the reference material and the abscissa is the specimen

temperature. Strella[13] has shown that the change in slope of the differential temperature between specimen and reference material in the region of the glass transition temperature is primarily a result of the change in specific heat of the specimen and that the glass transition temperature should be taken as the midpoint of this region. The specific heat is also approximately a linearly increasing function of temperature both above and below this transition region. Therefore, as shown in Figure 5, the temperature trace has been approximated by straight lines in the temperature range above and below the transition region with a third straight line through the inflection point of the transition region. The glass transition temperature was then taken as the midpoint of the two intersections of the straight line approximations, as indicated in Figure 5. The reproducibility of these curves decreases with increasing plasticizer content because of the decrease in magnitude of the differential temperature as the specimen temperature is increased through the transition region. Thus, the midpoint of the transition is reproducible to $\pm 1/2^{\circ}$ C with no plasticizer present but decreases to a reproducibility of approximately $\pm 2^{\circ}$ C with the maximum plasticizer content reported here.

Typical torsional pendulum results obtained for the PMMA-DEP system are shown in Figure 6. The ordinate is the logarithmic decrement, Δ, which is defined as the natural logarithm of the ratio of amplitudes of successive oscillations of the freely damped torsional pendulum and the abscissa is the specimen temperature. All points on the logarithmic decrement curves were reproducible to within $\pm 1^{\circ}$ C.

A dynamic glass transition temperature was arbitrarily defined as the point on the curves of Figure 6 where $\Delta = 0.9$. The reasons for

selecting this particular value of the logarithmic decrement will be discussed in the section on monomer plasticized PMMA. This definition is different from the normal[14] dynamic glass transition temperature which is taken as the temperature where the damping peaks. The peak in the curve was not obtained in these tests because the damping became too great to allow calculation of Δ by this method as the temperature was increased through the transition region. It may be seen from Figure 6 that an increase in the amount of plasticizer produces a shift to the left of the logarithmic decrement versus temperature curve and that the shape of the curve in the region of the glass transition temperature remains constant. The increased damping shown by the lower temperature part of the 16% DEP in PMMA curve is consistent with the behavior shown by Schmeider and Wolf[15] and does not invalidate use of the curve in the transition region. However, at somewhat higher plasticizer concentrations, the slope in the transition region would be expected to decrease,[15] corresponding to a broadening of the curve in the transition region. In such an instance, this method of determining glass transition temperatures would overestimate the glass temperature depression.

The glass transition temperatures, as measured by the three methods, are summarized in Table III. As expected, glass transition temperatures as measured by the DTA and torsional pendulum methods differ from the accepted dilatometrically determined glass transition temperatures because of the heating rate[13] and frequency[16] dependence of these methods, respectively. This difference was found to be quite constant with increasing plasticizer content. The DTA method at a heating rate of 5° C/min. gave glass temperatures approximately 4° C higher than those determined

dilatometrically, and the torsional pendulum glass temperatures at $\Delta = 0.9$ were about 6° C higher. These relations will be used in determining the true dilatometric glass transition temperature of the PMMA system from the dynamic glass transition temperature.

Glass Transition Temperature Measurements on Monomer Plasticized PMMA

The three methods used for measuring the glass transition temperature of the PMMA-DEP systems were also used to study the PMMA-MMA systems. Although a pseudo glass transition temperature may be measured by each of these methods, it is difficult to relate this temperature to the true glass transition temperature. This difficulty occurs because of the apparent rapid change in the rate of polymerization in the region of the glass transition temperature. Evidence of this polymerization will be seen in results obtained by each of the three methods. Therefore, as will be explained below, varying degrees of confidence will be placed on the validity of the indicated transition temperatures.

Typical dilatometer results are shown in Figure 7 for PMMA containing 0%, 1.1%, and 3.8% MMA. Here, the height of the dilatometer confining fluid (silicone oil) is plotted against temperature. It may be seen that the two lower curves do not behave in a manner similar to the PMMA-DEP system in which the slope of the dilatometer height versus temperature curve was essentially constant below the transition region and gradually increased through the transition to a higher constant value above the transition region. In Figure 7 the initial decrease in slope shown in the region where the lines are dashed is a result of the volume contraction

caused by polymerization of some of the monomer in the sample. Evidence of the extent of this polymerization are given below in connection with the DTA and torsional pendulum results. The temperature at which evidence for polymerization was first detected was reproducible to within 1° for any initial concentration of MMA. Although this temperature does decrease with increasing monomer content, as would be expected, it appears to be principally an indicator of the temperature at which the polymerization rate increases significantly. This break temperature is shown in column 4 of Table I. Thus, definition of an accurate glass transition temperature from dilatometric measurements would depend on knowing more about the relation between rate of polymerization and glass transition temperature.

Typical DTA traces for PMMA containing various concentrations of MMA are shown in Figure 8. It may be seen that with increasing monomer concentration, the traces develop an increasingly larger hump in the exothermic direction. To verify that this exothermic reaction was caused by polymerization, several of the samples were cooled after a DTA run to 0° C while still in the heating block. The experiment was then rerun under the same conditions. In all cases, the second run produced a trace nearly coincident with that of the completely polymerized sample in the transition region and showed no evidence of the exothermic hump. The areas under the curve might be expected to be related to the total quantity of heat produced by the polymerization, which is proportional to the amount of monomer in the sample. This was observed qualitatively; however, the instrument was not designed to give quantitative data.

The approximate temperatures in Figure 8, where the exothermic hump diverges upward from the ordinary DTA trace, have been marked. These

"upturn" temperatures were taken as DTA glass transition [illegible] the PMMA-MMA samples and are summarized in column 5 of Table I. [illegible] definition of an upturn temperature for the PMMA-MMA system is equivalent to the "midpoint" temperature for the PMMA-DEP system. These upturn temperatures were reproducible within ±2° C. Although these temperatures decrease with increasing plasticizer content, they also depend on the temperature at which the polymerization rate becomes significant and thus may be only indirectly related to the glass transition temperature.

The results obtained with the torsional pendulum for samples of PMMA containing monomer are shown in Figure 9. As was expected from Figure 6, the initial upturn portions of the Δ versus T curves shift in the direction of lower temperatures as the concentration of monomer is increased. The curve obtained for unplasticized PMMA agrees with the results of Nielsen,[14] which are also shown in Figure 9. The portion of the 4.6% and 12.0% MMA curves to the right of the inflection point on the ascending portion of the curve have been shown as dotted lines to emphasize the fact that the composition of these samples was changing during the latter part of the experiment. This was proven by I. R. analysis for monomer which was conducted before and after the experiment and indicated that monomer content decreased to less than 0.5%.

To prove that the change in monomer concentration was not caused by diffusion of the monomer to the surface followed by evaporation, a torsional pendulum specimen was subjected to a heating cycle identical to the heating cycle in the torsional pendulum experiment. The total weight loss during this cycle for the specimen which initially contained 12.0% monomer was less than 1/2%.

As previously noted in the PMMA-DEP section, the [illegible] transition temperature was defined as the temperature at [illegible]. This position on the damping curve was somewhat arbitrarily chosen as the glass transition temperature since at this damping level the shape of the curve had not changed as a result of polymerization. It is also high enough to be unaffected by any possible changes in the level of Δ at lower temperatures. To verify this assumption, three specimens from a sample containing 1.9% MMA were placed in an oven at 95° C for 10, 20, and 30 minutes. The MMA concentrations, as determined by I. R. analysis after removal from the oven, were identical with the initial concentration within experimental error. This indicates that the sample composition had not changed in time intervals comparable to the test time. The glass transition temperatures obtained using the torsional pendulum were reproducible to within ±1° C and are summarized in Table I.

The method described here for determining a glass transition temperature from the damping curve has an important advantage over the dilatometric and DTA methods in that the determination of the glass transition temperature is dependent only on the behavior at temperatures slightly above the true glass transition temperature. Thus, in the PMMA-MMA system, it is possible to measure a glass transition temperature free of the complications of polymerization. For this reason, the most confidence is placed in the accuracy of the glass transition temperatures measured by the torsional method, although those measured by the other two methods certainly give good indications of the magnitude of glass temperature depression with increasing monomer content.

DISCUSSION

Molecular Weight and Stereoregularity

The glass transition temperature of PMMA can be significantly affected by the presence of low molecular weight polymer[17] and by the stereoregularity of the polymer[18,19] as well as by the presence of plasticizers. Consideration has been given to whether or not the first two factors mentioned could significantly affect the results of this study, which is primarily concerned with plasticizer effects. For the reasons given below, the effects of molecular weight and stereoregularity on T_g are expected to be negligible compared to the effects of plasticizer for the current study.

The molecular weight data, given in Table II, show that the molecular weights of the unplasticized PMMA samples used in this work were high enough that effects on T_g could be safely neglected.[17] Moreover, the measured glass transition temperature of 108° C for the unplasticized PMMA prepared in this work is at least as high as the accepted value[20] of 105° C for PMMA prepared by a free radical mechanism. These results indicate that very little low molecular weight polymer was formed in the bulk polymerizations used in this work.

As pointed out in the literature, the stereoregularity of PMMA has a significant effect on the glass transition temperature. Predominantly isotactic[19] PMMA has a T_g of 45° C and predominantly syndiotactic[19] PMMA has a T_g of 115° C; whereas PMMA polymerized at temperatures from 40° to 60° C by a free radical mechanism[18,20,21] has a T_g of 104° to 106° C. The tacticity of PMMA polymerized by the free radical mechanism

depends only on the temperature of polymerization.[10,22] The polymer in all DEP-PMMA samples is expected to have similar stereoisomeric structures, since all samples were polymerized at the same temperatures. For the MMA-PMMA samples, however, only 85% of the polymer was formed at the same temperature (40° C). Hence, in this case the stereoregularity of about 15% of the polymer sample is subject to a change in stereoisomeric structure because of a change in the temperature of polymerization. This could lead to a consequent change in T_g.

An attempt was made to determine experimentally by N.M.R. spectra[10] the stereoregularity of the PMMA mixtures prepared for this work. The results of the N.M.R. structure analysis for three of the MMA-PMMA samples are given in Table II. These results compare favorably with the range of P_h/P_s values given by Fox and Schnecko[10] and Bovey[22] for polymerizations carried out in the temperature range of 40° to 100° C and are within the experimental scatter of P_h/P_s values for samples[10] polymerized at 60° C with AIBN. Therefore, because our measured P_h/P_s values fall within the range of the P_h/P_s values for polymers prepared by the conventional free radical process, the glass temperature of our polymer would also be expected to be similar to that of the conventional material (T_g ≐ 104° to 106° C) and the changes in T_g noted in this investigation are attributed only to the changes in plasticizer concentration.

Glass Transition Temperatures of DEP-PMMA Systems

The glass temperatures of PMMA containing various concentrations of DEP were determined by three different methods to inter-relate the glass transition temperatures obtained by each method and to compare the results,

where possible, with those reported in the literature.[5] Although these relations[23] are usually compared to glass temperatures which have been determined by volume dilatometry, it was of interest to relate glass temperatures determined by the less laborious DTA and torsional pendulum methods to the dilatometric T_g. The relation between the glass transition temperature as determined by the three methods is shown in Figure 10, where the glass transition temperature is plotted against DEP concentration. It should be noted that the dilatometric glass temperature is about 6° C lower than the torsional pendulum result and about 4° C lower than the DTA value.

The relatively constant difference between the torsional pendulum transition temperatures at $\Delta = 0.9$ and the dilatometric results for the DEP plasticized systems tends to support the assumption that the breadths of the torsional pendulum dispersion curves do not increase significantly with increasing DEP concentration in the concentration range of this investigation.

Glass Transition Temperatures of MMA-PMMA Systems

For monomer plasticized samples of PMMA it was found that the occurrence of a polymerization reaction at a rapid rate in the region of the glass transition temperature complicated the interpretation of the dilatometric and DTA methods for determining glass temperature. The pseudo glass transition temperatures measured by the three methods are plotted in Figure 11 against MMA concentration. The DTA upturn and dilatometric glass transition data show a large amount of scatter because of the polymerization reaction which occurred in MMA plasticized samples. The torsional

pendulum transition temperature was defined so that it was not affected by composition changes caused by the polymerization reaction. [illegible] transition temperatures determined by this method are considered to be valid. By analogy to what was found in the study of the DEP-PMMA system, it is expected that the true dilatometric glass transition temperatures, which should be used to test theoretical predictions, would lie about 5° C below the torsional pendulum results. This is because the major constituent of both the DEP-PMMA and MMA-PMMA systems is PMMA; therefore, the frequency dependence of the dynamic T_g measurement relative to the dilatometrically determined T_g should be principally a function of the PMMA and, thus, the same in both systems. This corrected T_g versus weight fraction of MMA is also shown in Figure 11.

Comparison of the results of the transition temperature measurements for the MMA-PMMA system shows that the DTA upturn temperatures for samples containing monomer are usually slightly lower than for the measured torsional pendulum results. This indicates that the DTA upturn is related to the glass transition temperature for the DEP-PMMA system. Since this upturn temperature is reproducible and has been related to the exothermic polymerization reaction which occurs in monomer plasticized PMMA, it means that the rate of polymerization becomes significant near the DTA glass transition temperature.

Based on the data shown in Table I, it may be seen that the true glass transition temperature is approximately 25° to 30° C above the sample polymerization temperature. The results of the rate experiment shown in Figure 1 show that at 80° C, which is close to the true glass temperature for a sample polymerized at 55° C, the rate of polymerization

is still insufficient to cause an appreciable change in [illegible] concentration during the time required for a glass temperature [illegible] ment. Thus, the rate of polymerization appears to increase [illegible] cantly between the true glass transition temperature and the [illegible] temperature.

The concept that a significant change in rate of polymerization takes place in the vicinity of the glass temperature is borne out by the results of Schultz and Harborth[24] who measured the rate of polymerization of MMA at constant temperature as a function of sample conversion. They found that the rate of polymerization decreased very markedly at a particular sample composition for each temperature studied. The composition-temperature relationship which they obtained agrees closely with our results. At 50°, 70°, and 90° C, Schultz and Harborth found that 14%, 8.5%, and 2.0% MMA remained unpolymerized in their samples; likewise, in this work a smooth curve drawn through the DTA upturn temperatures given in Table I gives the same three sample compositions within experimental scatter for the above three temperatures. Loshaek and Fox[25] postulated that in a polymerizing system the polymerization will proceed until the composition of the monomer-polymer mixture has a glass temperature equal to the polymerization temperature. The current work indicates that, although the rate of polymerization does decrease markedly when the temperature is lowered through the T_g of the mixture, further polymerization does occur below the glass transition temperature of a MMA-PMMA solution. This marked change in rate which occurs at a temperature slightly above the true glass temperature in the MMA-PMMA solutions is probably related to a rapid change in the diffusion of monomer within the

sample at this temperature or to a marked change in t[illegible] diffusion-controlled initiator decomposition reaction.

The fact that the dilatometric break temperatures for the MMA-[illegible] system are usually higher than the DTA upturn temperatures [illegible] containing MMA can probably be attributed to the greater sensitivity of the DTA method in detecting the polymerization reaction. Also the fact, that for samples containing MMA the dilatometric break usually indicates higher transition temperatures than the torsional pendulum, is further proof that the MMA-PMMA sample composition does not change significantly up to temperatures at which $\Delta = 0.9$.

Comparison of Results With Available Data and Analyses

The measured glass transition temperatures as a function of diluent content were compared with T_g predicted by three available relations for glass transition temperature depression due to increasing plasticizer content. The first of these relations is due to Fox[2] and is similar in concept to the Gordon-Taylor[3] relation for glass transition temperature of a copolymer. Fox's expression has the form:[2]

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \qquad (1)$$

where T_{g_1} and T_{g_2} represent the glass transition temperatures of the pure polymer and pure diluent, respectively, and W_1 and W_2 are their respective weight fractions in the system.

The second relation for the glass transition temperature of a polymer-diluent system is derived from the iso-free volume concept of the glass

transition temperature and the assumption of additivity [illegible] of polymer and diluent. This relation, as given by Kelley [illegible] has the form:[23]

$$T_g = \left[\alpha_p v_p T_{gp} + \alpha_d(1 - v_p)T_{gd}\right] \Big/ \left[\alpha_p v_p + \alpha_d(1 - v_p)\right] \qquad (2)$$

where T_g is the glass temperature of the polymer-diluent system, T_{gp} is the glass temperature of undiluted polymer, T_{gd} is the glass temperature of diluent, v_p is the volume fraction of polymer in the solution, and α_p and α_d are defined as the difference in the thermal expansion coefficients in the liquid and glass states of the polymer and diluent, respectively.

Gibbs and Dimarzio[26] consider the glass-transition temperature to be related to a thermodynamic second-order phase transition which is predicted by their statistical mechanical theory, even though relaxation effects prevent attainment of a true second-order transition temperature. These authors[5] make use of a quasi-lattice model and allow for rotational energy states in the molecules to derive an expression for the glass-transition temperature of a polymer-diluent system. For a high molecular weight polymer containing a volume fraction of diluent, v, the glass temperature can be obtained from the following Dimarzio-Gibbs[5] equation:

$$\frac{1}{1 - v} \ln\left(\frac{r_B + v}{2r_B}\right) + \frac{v}{r_B(1 - v)} \cdot \ln\left[\frac{6(r_B + v)}{2v}\right] + \ln(1 + 2e^{\beta_1}) + \frac{2\beta_1 e^{\beta_1}}{1 + 2e^{\beta_1}} + \frac{v(r_B - 3)}{r_B(1 - v)}\left[\ln(1 + 2e^{\beta_2}) + \frac{2\beta_2 e^{\beta_2}}{1 + 2e^{\beta_2}}\right] = 0 \qquad (3)$$

where $\beta_1 = -\Delta\epsilon_A/kT_g$; $\beta_2 = -\Delta\epsilon_B/kT_g$; r_B is the number of [illegible] that a plasticizer molecule occupies; k is Boltzmann's constant; T_g is the glass temperature of the polymer-diluent system; and $\Delta\epsilon_A$ [illegible] are the average stiffness energies by which one of three possible rotational positions about a bond of the model is favored in the polymer and the diluent molecules, respectively. Empty lattice sites (free volume) are not taken into account in Equation (3). However, the effect of empty lattice sites on the calculations has been described.[26]

If $v = 0$ in Equation (3), $\Delta\epsilon_A$ can be computed by substituting for T_g the experimental values of the glass temperature for undiluted polymer. Hence, the Dimarzio-Gibbs equation gives the glass temperature of a polymer-diluent system as a function of the length of the diluent molecule (r_B), its stiffness energy ($\Delta\epsilon_B$), and concentration (v).

In Figure 12, the dilatometer results obtained for the DEP-PMMA systems are plotted as T_g versus weight fraction of DEP and compared with predictions of Equations (1), (2), and (3). Some points from the low concentration end of the Kelley-Bueche[4] data are also plotted in this figure. The measured T_{g_1} of 381° K and the value of T_{g_2} of 208° K reported by Kelley and Bueche[4] were used in relation (1). The Kelley-Bueche relation (2) was arbitrarily fitted to the experimental dilatometric glass temperature data at low DEP concentrations by treating α_d in Equation (2) as an adjustable parameter. The other parameters in Equation (2) were given their experimental values; T_{gp} was taken as 381° K; Rogers and Mandelkern's[20] value of $\alpha_p = 2.45\times10^{-4}$ deg^{-1} was used, and again $T_{g_2} = T_{gd} = 208°$ K for DEP. A value of

$\alpha_d = 4.0 \times 10^{-4}$ deg^{-1}, which is in the range expected for [illegible] was found to fit the data well. To plot the theoretical [illegible] curve (Eq. (3)), the assumption that the polymer and dilu[illegible] same stiffness energy, that is, $\Delta\epsilon_A = \Delta\epsilon_B$, was made, and [illegible] equal to 9 for the following reason: From theory[5] a monom[illegible] PMMA occupies four lattice sites. Hence, the volume of a mole of [illegible] is about 21.2 ml. Comparing this with the molar volume of DEP shows that a molecule of DEP would occupy about nine lattice sites. For the low concentrations of DEP of current interest (16% or less) all three relations describe the experimental data adequately.

In Figure 13, the true glass temperatures for the MMA-PMMA solutions, which were obtained by subtracting 6° C from the torsional pendulum results in Table I, are plotted against weight fraction of MMA. Curves from relations (1), (2), and (3) are also plotted on this figure. The value of T_{g_2} and T_{gd} used in expressions (1) and (2) was estimated to be about 153° K by a graphical extrapolation of the results of Alexandrov and Lazurkin.[27] This value for T_{g_2} and T_{gd} may be in error as much as ±10° C because of the extrapolation and the unknown frequency or temperature dependence of Alexandrov and Lazurkin's method of measuring T_g. However, the effect of this error in calculations of T_g will be small for the low concentrations of monomer of interest here. Thus, relation (1) is plotted with $T_{g_2} = 153°$ K. Using this value for T_{gd} and the same values of T_{gp} and α_p given above in the discussion of DEP results, a value of $\alpha_d = 5.0 \times 10^{-4}$ deg^{-1} was chosen to arbitrarily fit relation (2) to the experimental data at 12% MMA. The Dimarzio-Gibbs curve shown in Figure 13 was computed from Equation (3) with r_B equal to 5 and the

stiffness energy of monomer taken equal to that of [illegible] the polymer chain, that is, $\Delta\epsilon_B = \Delta\epsilon_A$. The value of ϵ_B [illegible] by comparing the volume of a lattice site to the molecular [illegible] MMA.

All three relations significantly underestimate the glass [illegible]ture depression at low concentrations of monomer. The rapid initial decrease in T_g as a function of monomer content for the PMMA-MMA system is apparently not unique, however, since similar behavior can be deduced from the results of Alexandrov and Lazurkin[27] for styrene-polystyrene solutions and of Mandelkern and Flory[28] for dimethyl phthalate-cellulose tributyrate solutions. From the references cited and from the data reported here, it would appear that this deviation from predicted behavior may be most prevalent for polymers plasticized with their own monomer.

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TABLE I

Results of Transition Temperature Determinations for the MMA-PMMA System

Polymerization conditions			Transition temperature, °C		
Time, days	Temperature,[a] °C	MMA conc. wt. fraction	Dilatometer break	DTA upturn	Tor. pendulum, Δ = 0.9
5	100	0	108	113	114
5	95	0	108	115	114
4	80	0.005	105	104	---
4	75	0.008	---	107	---
4	70	0.010	---	97	101
4	65	0.011	93	91	---
4	61	0.019	---	90	91
4 and 4[b]	44 and 55[b]	0.024	---	84	89
4	55	0.029	86	84.5	---
7	50	0.038	81	75.5	---
7	44	0.046	80	-	78
7	40	0.069	---	73	---
7	36	0.082	67	63	---
7	30	0.12	---	48	55

[a]All samples were polymerized at 40° C for 24 hrs. prior to being subjected to the temperatures given in this column.

[b]This sample was heated 4 days at 44° C and then at 55° C for an additional 4 days.

TABLE II

Molecular Weight and N.M.R. Data for PMMA

Polymerization temperature, °C	Percent conversion	$\bar{M}_v \times 10^{-6}$ (g/mole)	$\bar{M}_n \times 10^{-6}$ (g/mole)	P_h/P_s
100	100	5.0	0.5	0.72
70	99	---	---	0.63
61	98	1.7	~1	---
48	96	4.3	~1	---
36	92	---	---	0.64

TABLE III

Results of Transition Temperature Determinations for the DEP-PMMA System

Wt percent DEP	Glass transition temperature, °C		
	Dilatometric	DTA midpoint	Tor. pendulum, $\Delta = 0.9$
0	108	113	114
3.0	---	105	107
3.6	99	105	105
8.0	84	89	91
16.0	65	73	69

FIGURE LEGENDS

Figure 1. Rate experiment for the bulk polymerization of MMA containing 0.5% AIBN. Initial polymerization conducted at 40° C for 24 hrs.

Figure 2. Schematic diagram of DTA instrument.

Figure 3. Schematic diagram of torsional pendulum.

Figure 4. Typical dilatometer results for DEP plasticized PMMA.

Figure 5. Typical DTA traces obtained at a heating rate of 5° C/min. for DEP plasticized PMMA.

Figure 6. Torsional pendulum results for DEP plasticized PMMA.

Figure 7. Typical dilatometer results for PMMA containing monomer.

Figure 8. Typical DTA traces for monomer plasticized PMMA obtained at a heating rate of 5° C/min.

Figure 9. Torsional pendulum results for monomer plasticized PMMA.

Figure 10. Glass transition temperatures as determined by three methods for DEP-PMMA samples.

Figure 11. Glass transition temperatures as determined by three methods for MMA-PMMA samples.

Figure 12. Comparison of experimental glass transition temperatures of DEP-PMMA systems with theoretical predictions.

Figure 13. Comparison of experimental glass transition temperatures for MMA-PMMA systems with the predictions of available theories.

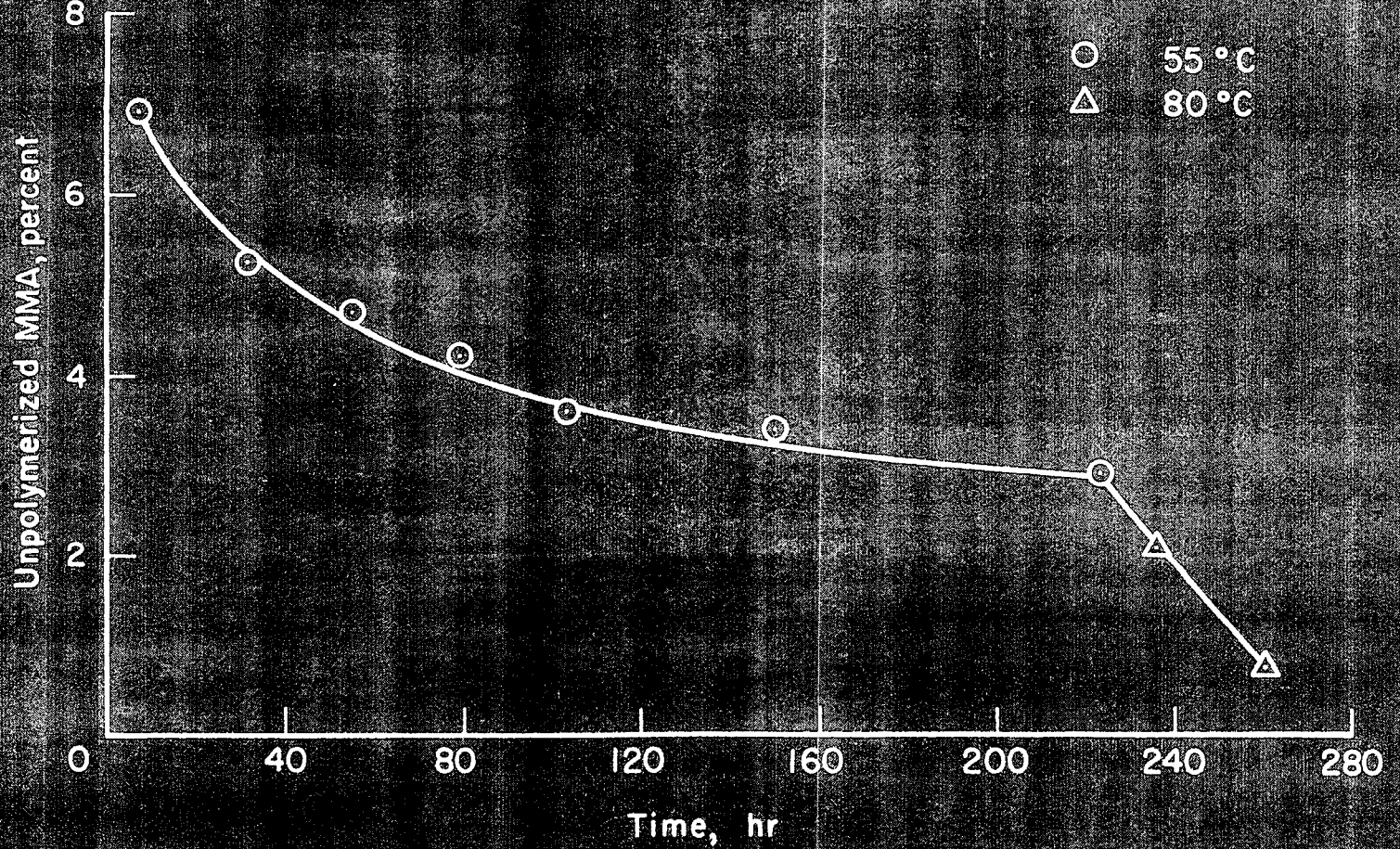

Figure 1.

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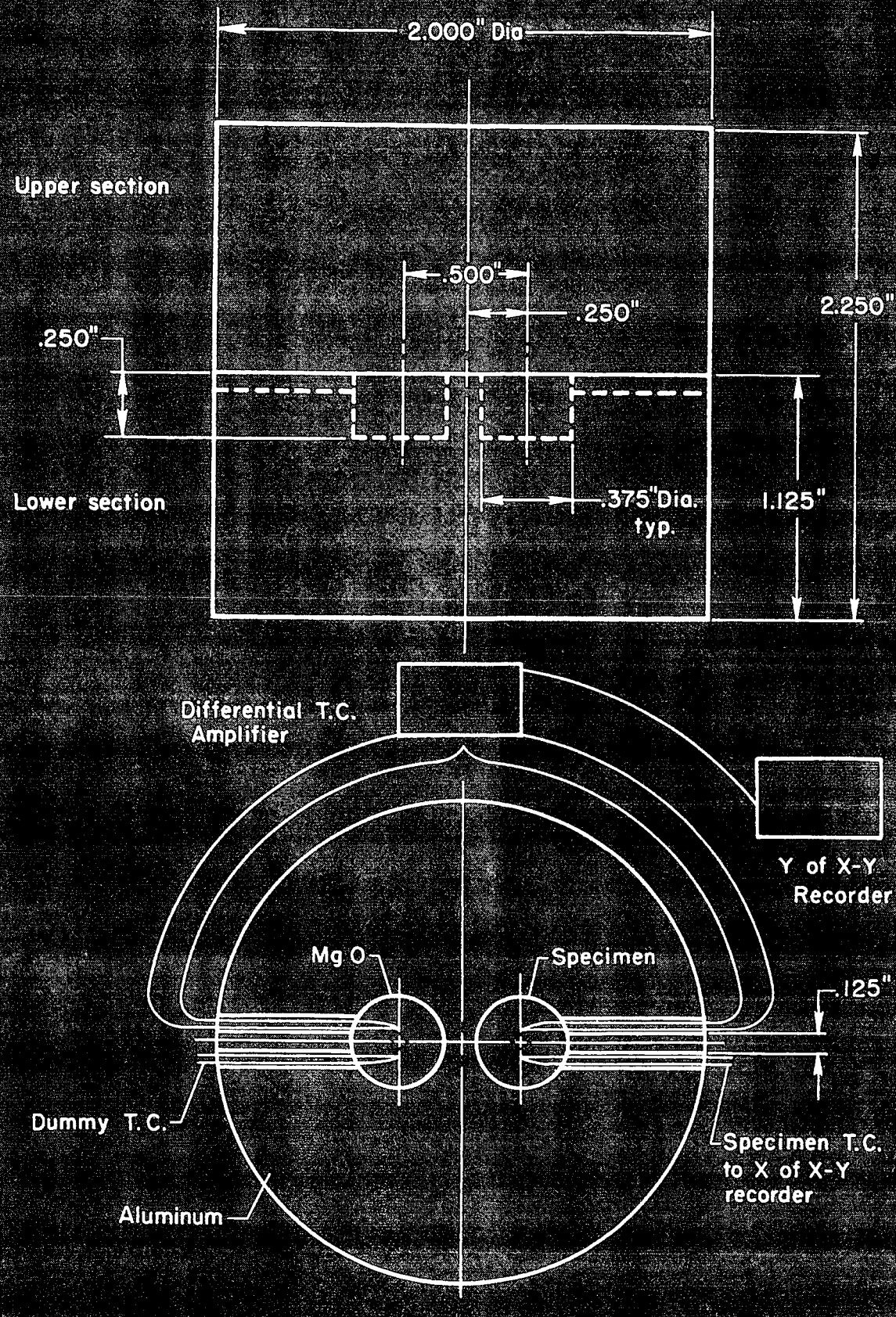

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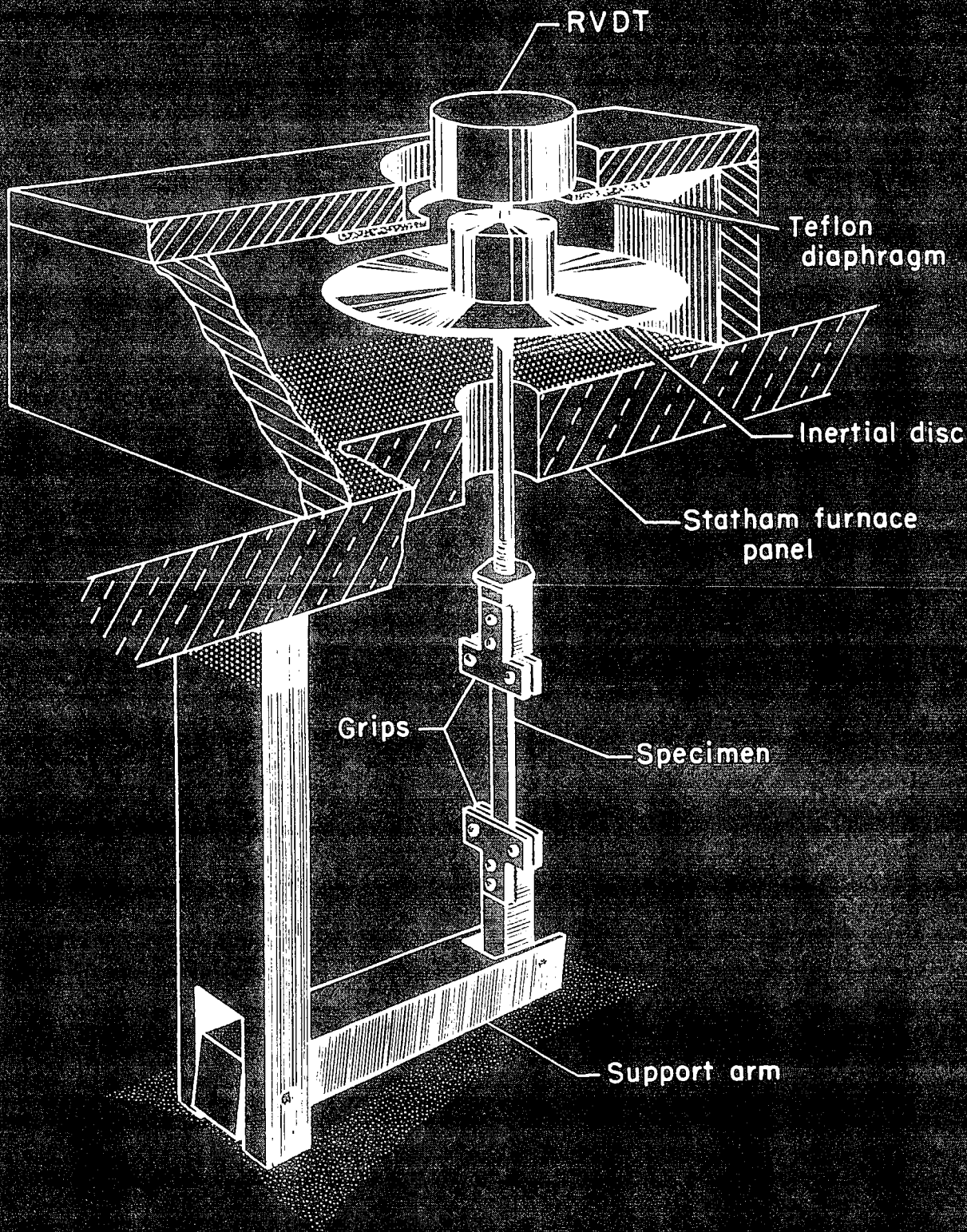

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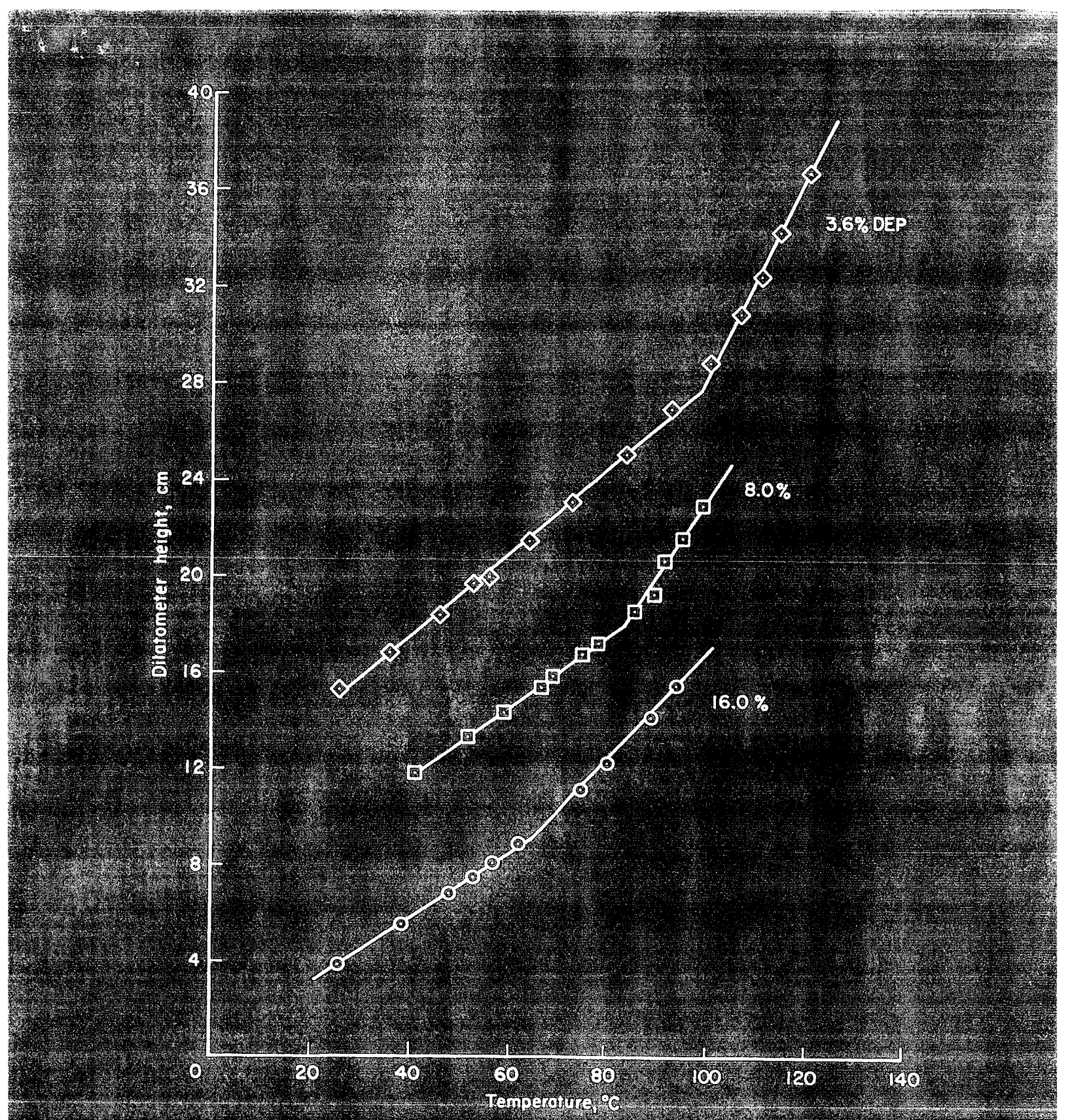

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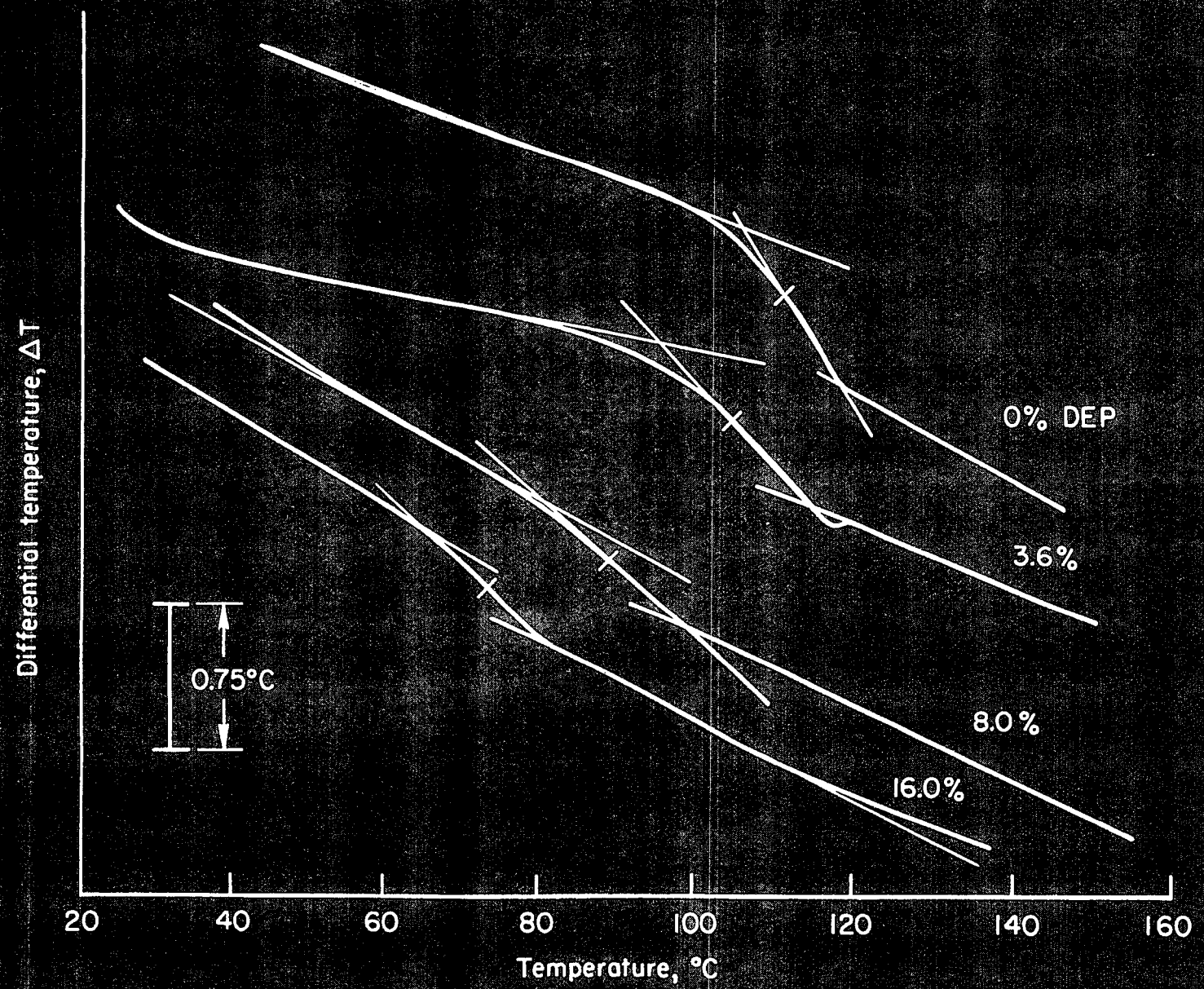

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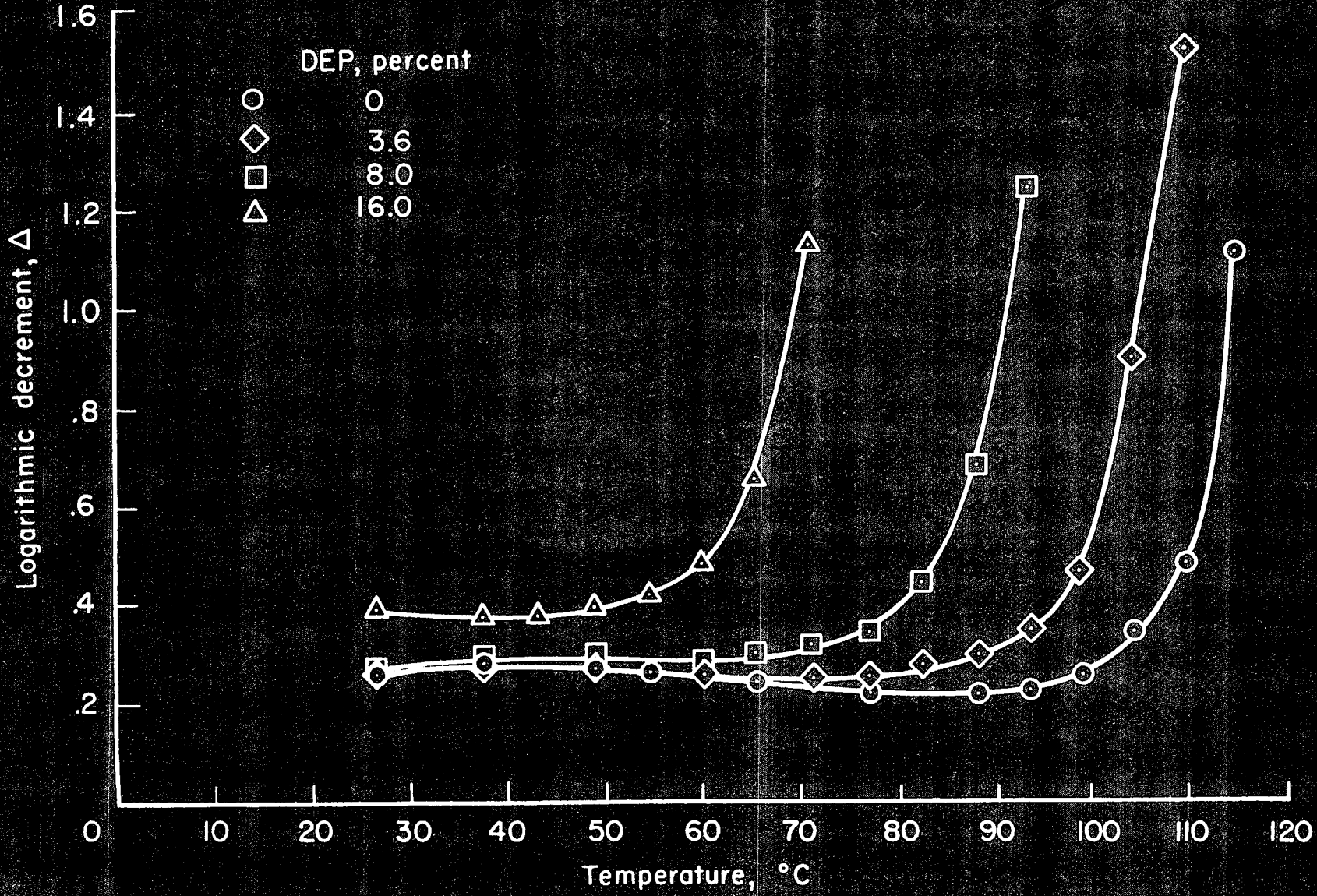

Figure 6.

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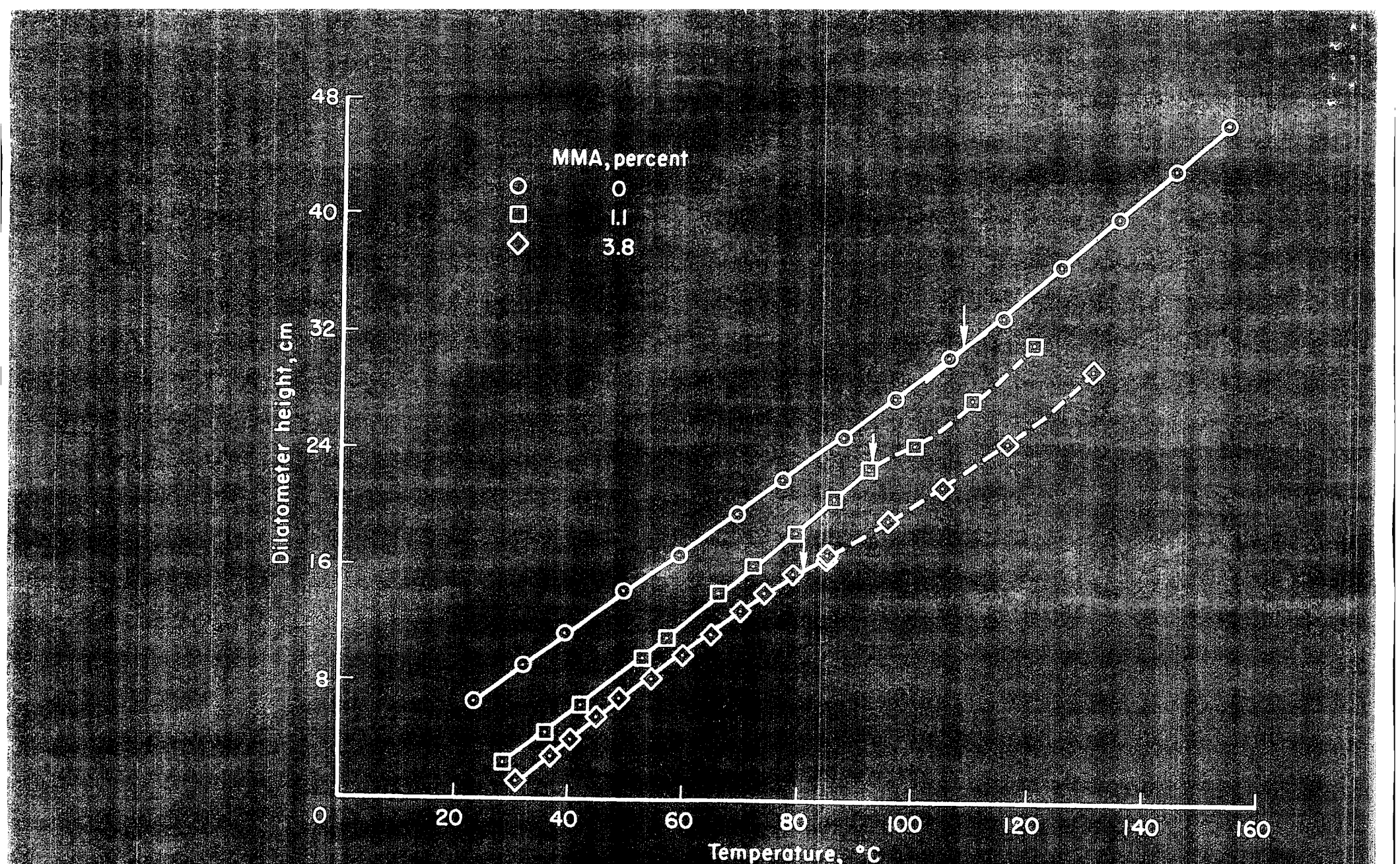

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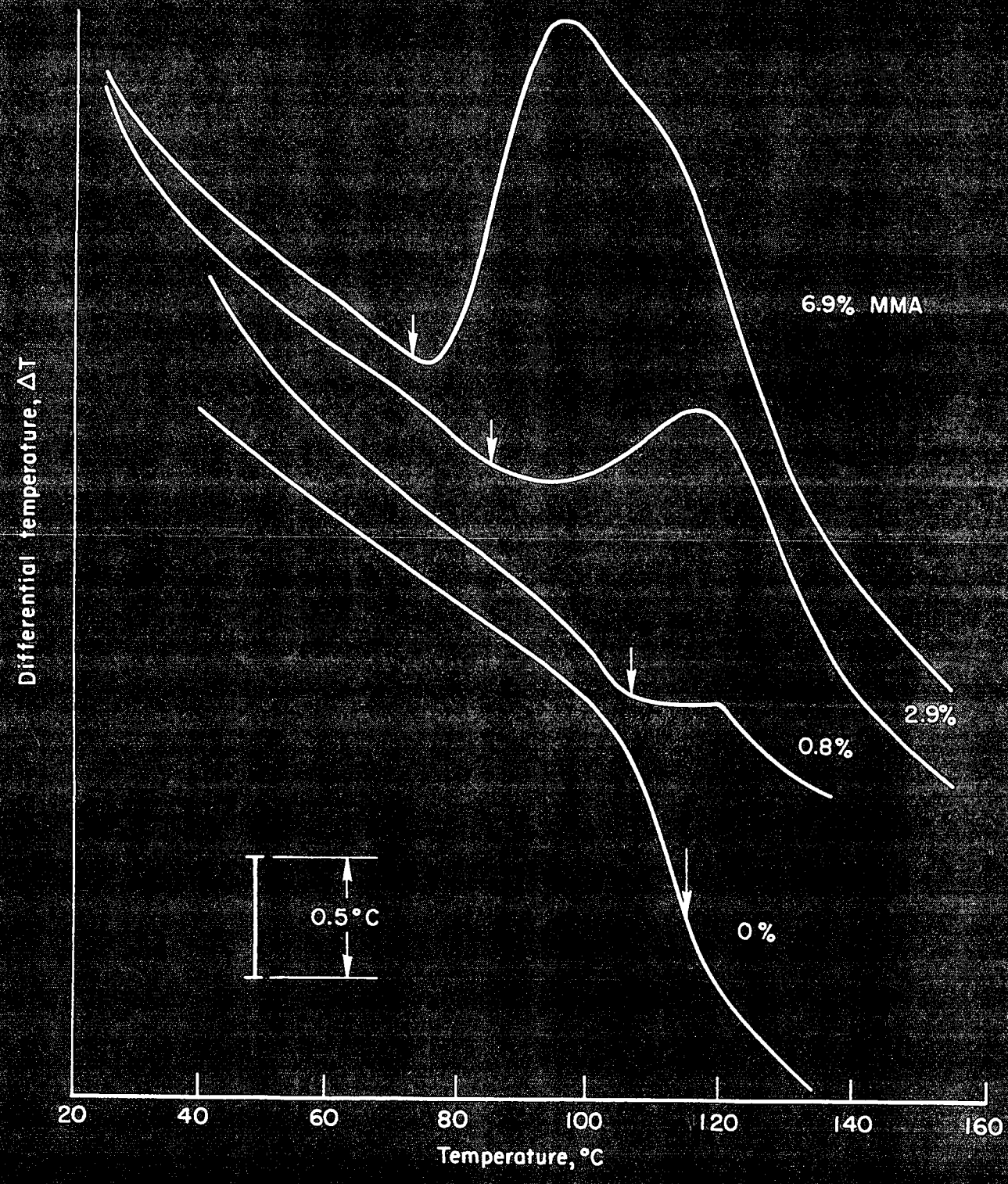

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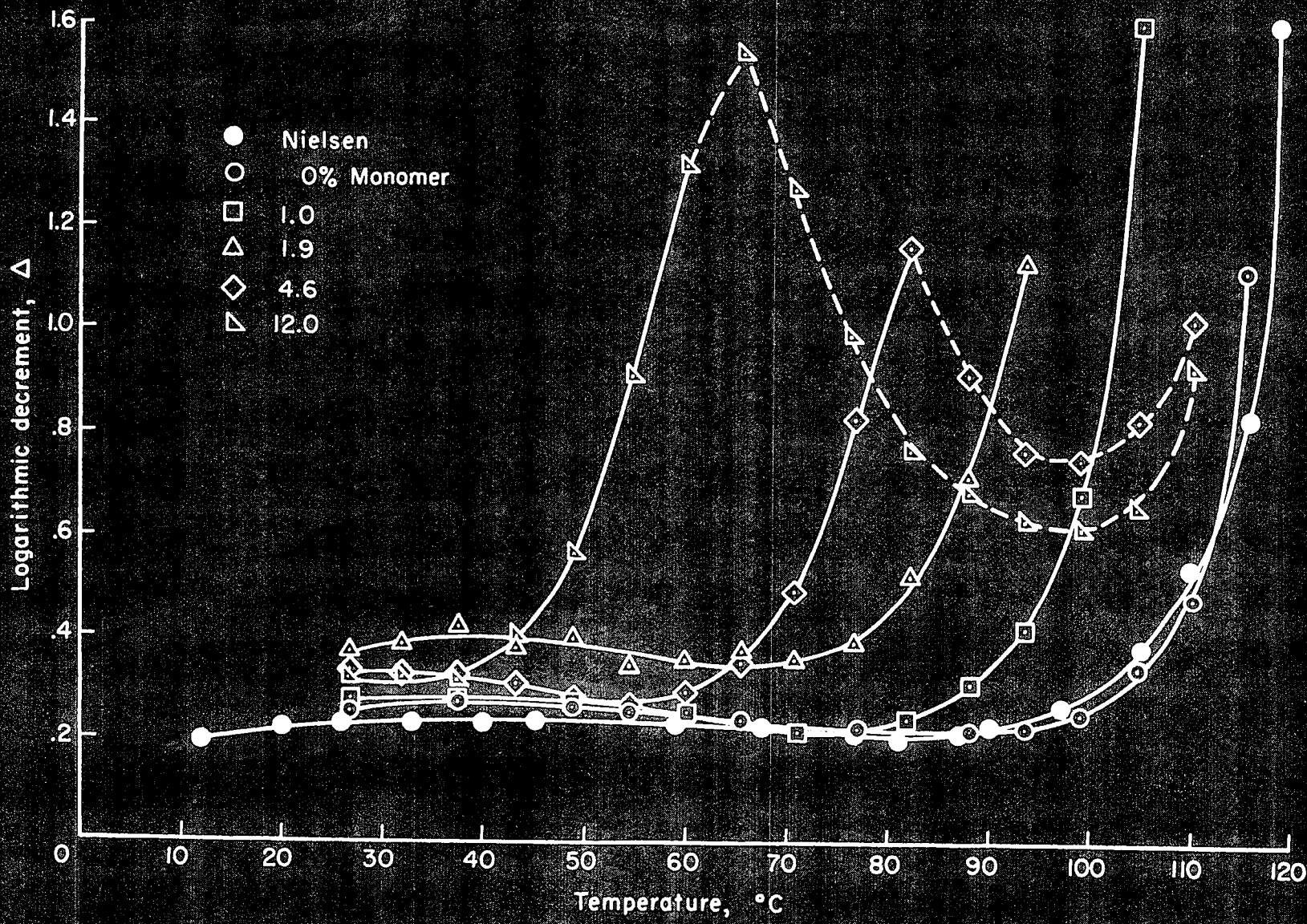

Figure 9.

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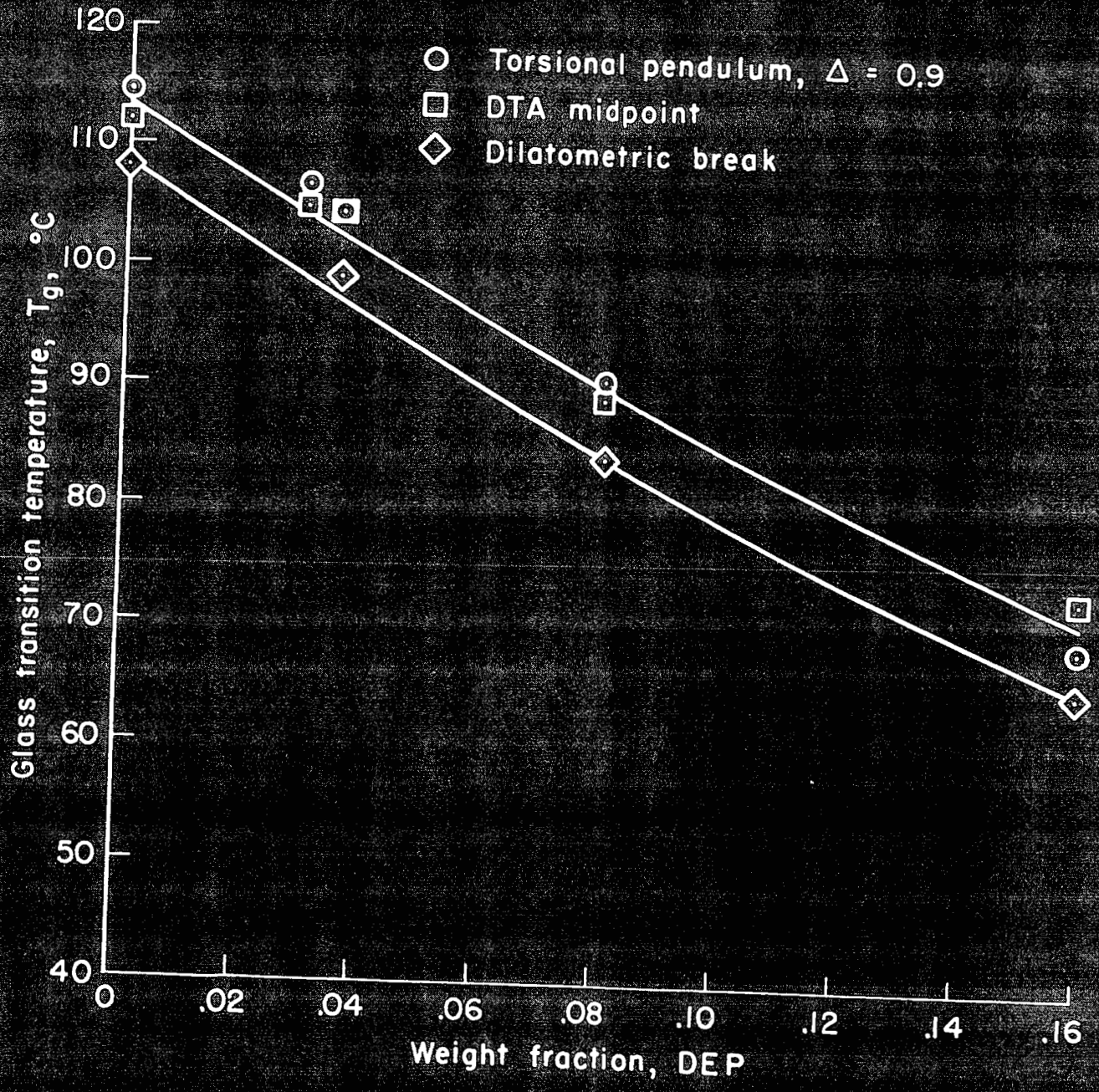

Figure 10.

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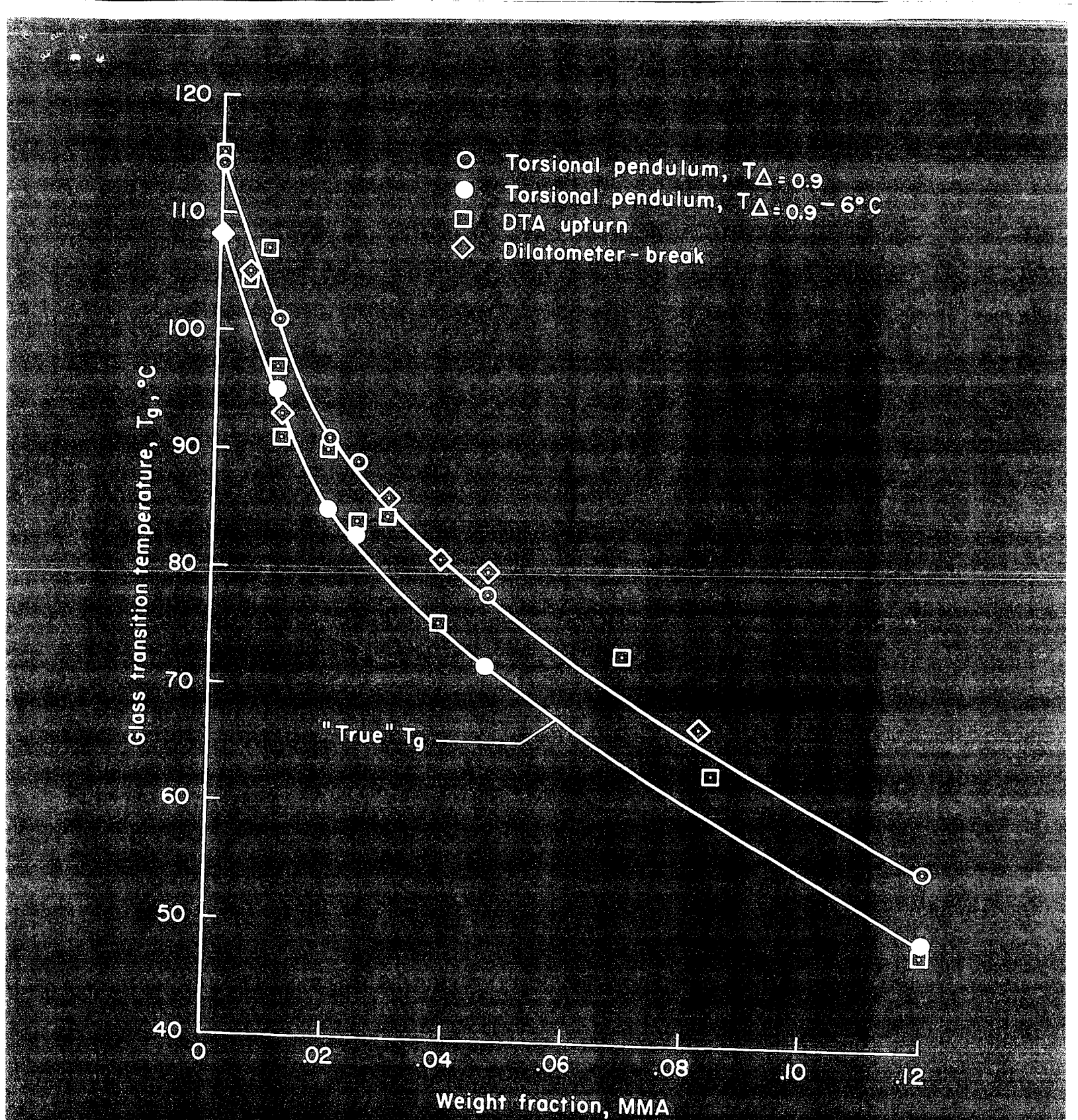

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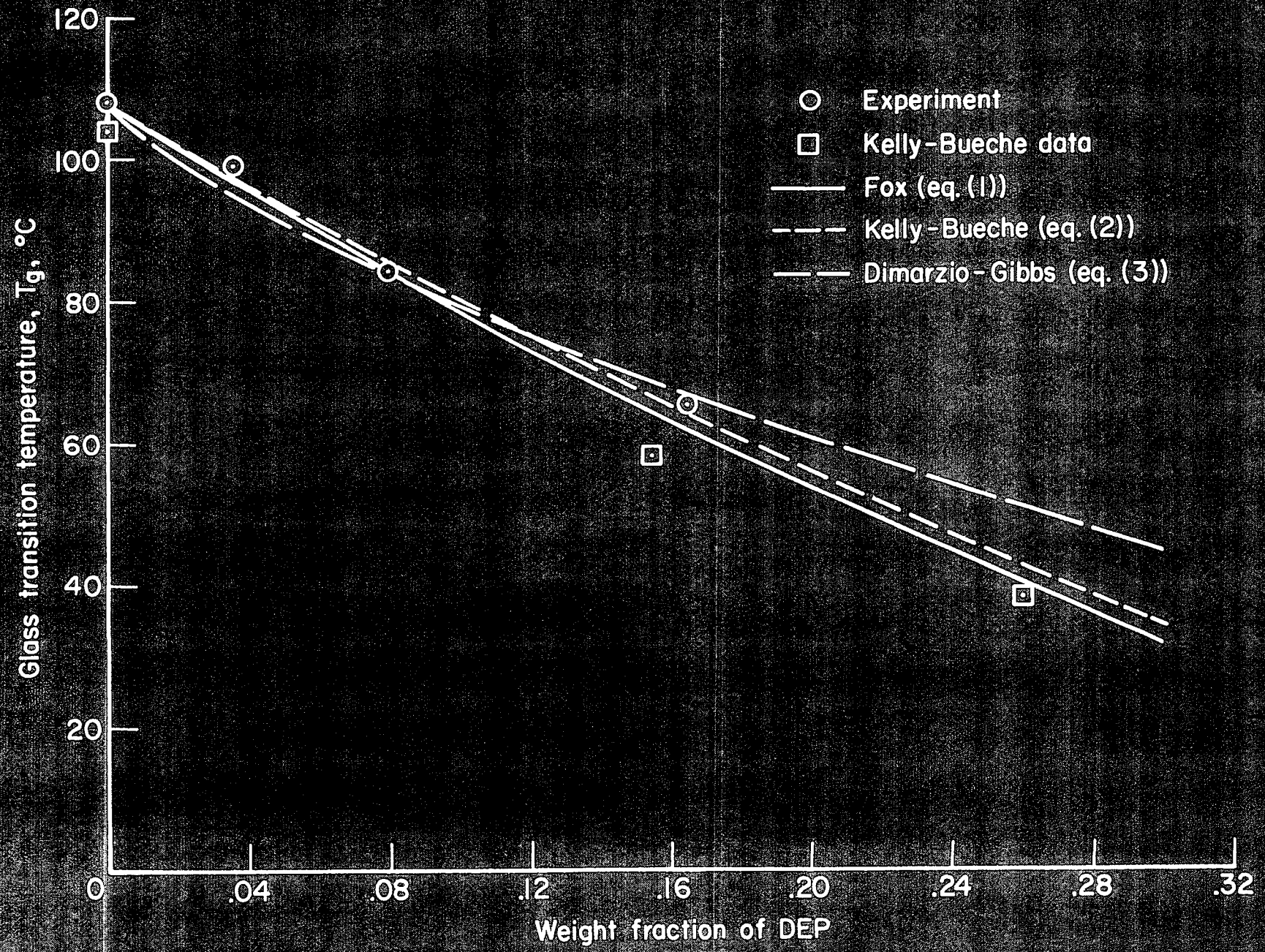

Figure 12.

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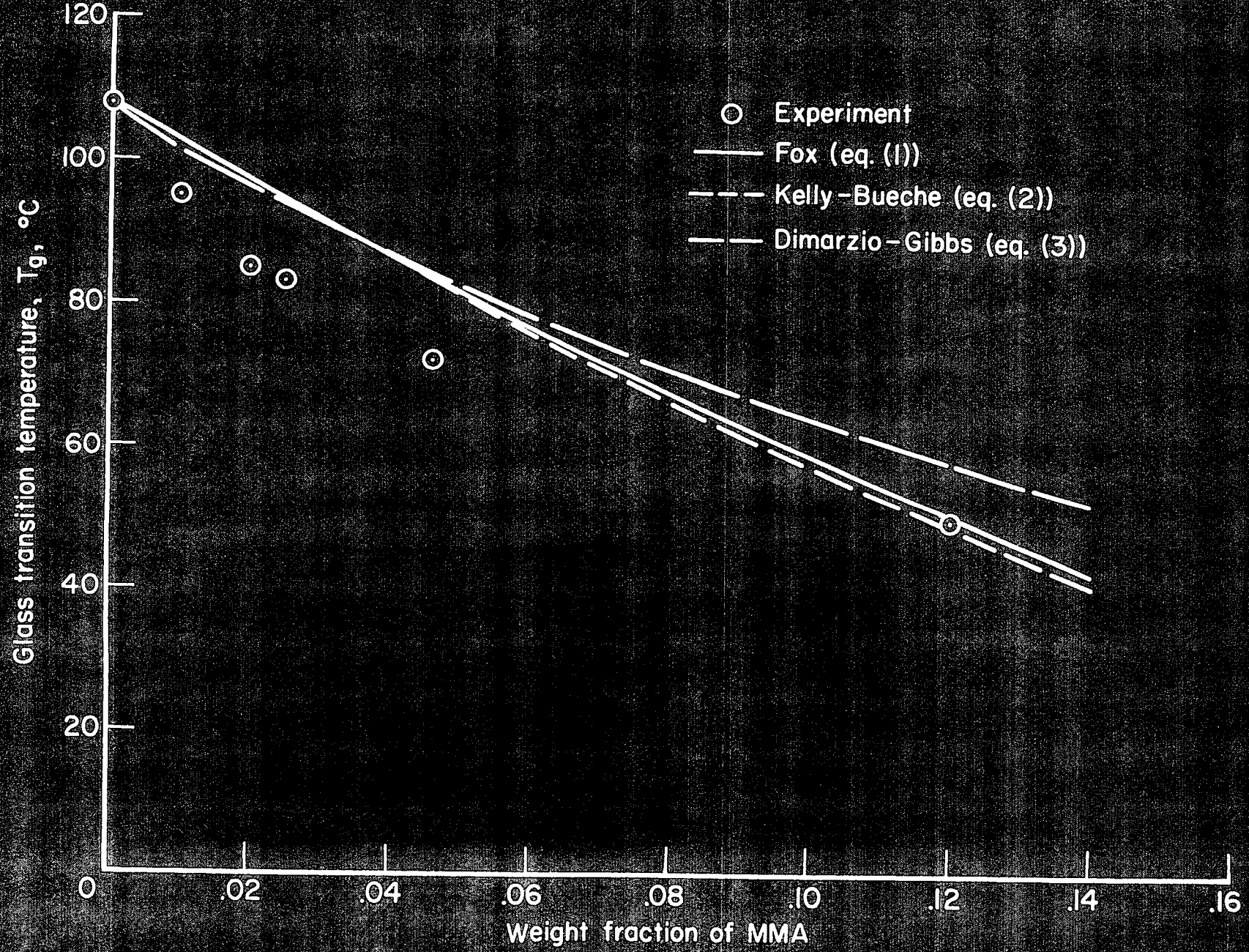

Figure 13.

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